

THE INTERNUCLEAR SEPARATION DERIVATIVES OF  
THE ENERGY OF A DIATOMIC MOLECULE

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ABSTRACT

General formulae for the higher order derivatives of the energy with respect to the internuclear separation of a diatomic molecule are derived from the Hellmann Feynman theorem and the Integral Hellmann Feynman theorem. The phenomenon of the cancellation of terms involving the charge density and its derivatives, which has been observed for the second order derivative by Salem, is shown to prevail for third and higher order derivatives. On this basis an approximate working formula is suggested. A new condition under which an approximate wave function satisfies the Hellmann Feynman theorem rigorously is given. With such an approximate wave function, the formulae for the general derivatives of the energy derived are also shown to be valid.

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## 1. INTRODUCTION

The derivatives,  $E^{(k)} = \left. \frac{d^k E}{dR^k} \right|_{R=R_0}$  where  $R_0$  is the equilibrium internuclear separation of the diatomic molecule, are the important physical constants in connection with molecular vibration. For instance,  $E^{(0)}$  is the binding energy,  $E^{(1)}$  is zero,  $E^{(2)}$  is the quadratic force constant, and  $E^{(3)}$  is the cubic force constant.

The usual treatments of the derivatives make use of the Hellmann Feynman theorem,<sup>1-4</sup> the perturbation theory<sup>5</sup>, or the quantum mechanical virial theorem.<sup>6</sup> Our present derivations of the general formulae of  $E^{(k)}$  are based on the Hellmann Feynman theorem<sup>1</sup> and the Integral Hellmann Feynman theorem<sup>7,8,9</sup>.

A general formula of  $E^{(k)}$  was given recently by Schwendeman<sup>4</sup> through the successive differentiation of the Hellmann Feynman theorem, by use of the body fixed coordinate system on one of the atoms. His final form<sup>10</sup> contains the derivative of the charge density with respect to the nuclear displacement. In the differentiation, the position vector of the observation point with respect to the atom is held constant.

In the present work, we employ the space fixed coordinate system in which one of the atoms is fixed. As a result one can visualize the relative importance of the various terms involved so that one can get more insight, especially when one seeks an approximate form.

In Sec. II, the derivations are given by use of the expansion of the integral of the type  $\int \frac{1}{r_A} f(r) d\tau$  in the power series of the nuclear displacement due to Bingel.<sup>11</sup>

In Sec. III, we discuss the cancellation between the terms involving the density and its derivatives. The emphasis is placed on  $E^{(3)}$  and an approximate form is suggested. In addition, we present the new prescription of "a stable wave function" by use of the Integral Hellmann Feynman theorem.

## II. FORMAL DERIVATION

### A. The Electrostatic Approach

According to the Hellmann Feynman theorem,

$$\frac{dE}{dR} = \langle \Psi | \frac{\partial H}{\partial R} | \Psi \rangle \quad (1)$$

the force acting on the nucleus A of the diatomic molecule, due to the other nucleus B and the surrounding electronic charges, is given by

$$\frac{dE}{dR} = -\frac{Z_A Z_B}{R_0^2} + Z_A \int \left( \frac{\partial}{\partial Z_A} \frac{1}{r_A} \right) \rho(r; Z_A) d\tau \quad (2)$$

where  $Z_A$  and  $Z_B$  are the nuclear charges of the atoms A and B, and  $\rho(r; Z_A)$  is the first order density normalized to N, the total number of electrons (see Fig. 1).

It should be emphasized that the nucleus B is fixed to the coordinate frame which itself is fixed in space.

We are interested in the higher order derivatives of the energy with respect to the internuclear separation at the equilibrium configuration,  $R = R_0$ . From the successive differentiation of both sides of the Eq. (2), one has

$$E^{(K)} \equiv \left. \frac{\partial^K E}{\partial R^K} \right|_{R=R_0} = (-1)^K K! \frac{\hat{\chi}_A \hat{\chi}_B}{R_0^{K+1}} + (-1)^{K-1} \sum_A \sum_{m=0}^{K-1} \binom{K-1}{m} \cdot \left[ \frac{\partial^{K-m}}{\partial z_A^{K-m}} \int \frac{1}{r} P^{(m)}(\mathbf{r}) d\mathbf{r} \right]_{z_A=0} \quad (3)$$

where  $P^{(m)}(\mathbf{r})$  is defined by

$$P^{(m)}(\mathbf{r}) \equiv \left[ \frac{\partial^m}{\partial z_A^m} P(\mathbf{r}; z_A) \right]_{z_A=0} \quad (4)$$

It can be shown<sup>11</sup> that, for an arbitrary function

$$\int \frac{1}{r} f(\mathbf{r}) d\mathbf{r} \equiv \int \frac{1}{r} f(r, \cos\theta) d\mathbf{r} = \sum_K z_A^K \left( \frac{4\pi}{2K+1} \int_0^\infty \hat{f}_K(r) r dr \right) + \sum_K \sum_n z_A^{K+n+2} \left( \frac{4\pi (-1)^{n+1} (n+1)}{(n+2)!(2K+n+3)} \hat{f}_K^{(n)}(0) \right) \quad (5)$$

where

$$\hat{f}_K(r) = \frac{2K+1}{4\pi} \int P_K(\cos\theta) f(\mathbf{r}) \sin^2\theta d\theta d\varphi \quad (6)$$

$$\hat{f}_K(r) = f_K(r)/r^K \quad (7)$$

$$\hat{f}_K^{(n)}(0) = \left[ \frac{\partial^n}{\partial r^n} \hat{f}_K(r) \right]_{r=0} \quad (8)$$

Thus, one obtains

$$E^{(K)} = (-1)^K K! \frac{\hat{\chi}_A \hat{\chi}_B}{R_0^{K+1}} + (-1)^{K-1} (K-1)! \sum_A \sum_{m=0}^{K-1} \frac{K-m}{m!} \left[ \int \frac{P_{K-m}(\cos\theta)}{r^{K-m+1}} \cdot P^{(m)}(\mathbf{r}) d\mathbf{r} - \sum_{q=0}^{K-m-2} \frac{(q+1)(2K-2m-3-2q)}{(q+2)!(2K-2m-1-q)} \int \frac{P_{K-m-q-2}(\cos\theta)}{r^{K-m-q}} \cdot \delta^{(q)}(r) P^{(m)}(\mathbf{r}) d\mathbf{r} \right] \quad (9)$$

where  $\delta^{(q)}(r)$  is the  $q$ -th derivative of the delta function<sup>13</sup>,

$$\int_0^\infty \delta^{(q)}(r) g(r) dr \equiv (-1)^q \left[ \frac{\partial^q g(r)}{\partial r^q} \right]_{r=0} \quad (10)$$

The first three derivatives are<sup>14</sup>

$$E^{(1)} = -\frac{\zeta_A \zeta_B}{R_0^2} + \zeta_A \int \frac{P_1(\omega R \theta)}{r^2} P^{(0)}(r) dT \quad (11)$$

$$E^{(2)} = 2\frac{\zeta_A \zeta_B}{R_0^3} - 2\zeta_A \int \frac{P_2(\omega R \theta)}{r^3} P^{(0)}(r) dT + \frac{\zeta_A}{3} \int \frac{\delta(r)}{r^2} P^{(0)}(r) dT - \zeta_A \int \frac{P_1(\omega R \theta)}{r^2} P^{(1)}(r) dT \quad (12)$$

$$E^{(3)} = -6\frac{\zeta_A \zeta_B}{R_0^4} + 6\zeta_A \int \frac{P_3(\omega R \theta)}{r^4} P^{(0)}(r) dT - \frac{9}{5}\zeta_A \int \frac{P_1(\omega R \theta)}{r^3} \delta(r) P^{(0)}(r) dT - \frac{1}{2}\zeta_A \int \frac{\delta^{(1)}(r)}{r^2} P^{(0)}(r) dT + 4\zeta_A \int \frac{P_2(\omega R \theta)}{r^3} P^{(1)}(r) dT - \frac{2}{3}\zeta_A \int \frac{\delta(r)}{r^2} P^{(1)}(r) dT + \zeta_A \int \frac{P_1(\omega R \theta)}{r^2} P^{(2)}(r) dT \quad (13)$$

Eq. (12) is the Salem's formula<sup>3</sup> for the quadratic force constant.

#### B. The Integral Hellmann Feynman Theorem

Suppose that:

$$(H-E)\Phi = 0 \quad (14)$$

$$(H_0-E_0)\Phi_0 = 0 \quad (15)$$

$$\Delta H = H - H_0 \quad (16)$$

The sum of the all orders of the perturbation energies, due to the perturbation  $\Delta H$  may be written by the Integral Hellmann Feynman theorem,<sup>7,8,9</sup>

$$E - E_0 = \frac{\langle \Psi | \Delta H | \Psi_0 \rangle}{\langle \Psi | \Psi_0 \rangle} = \gamma_A \gamma_B \left( \frac{1}{R} - \frac{1}{R_0} \right) + \gamma_A \int \left( \frac{1}{r_A} + \frac{1}{r} \right) \sigma(\mathbf{r}; \mathbf{z}_A) d\mathbf{r} \quad (17)$$

where the last equality is based on the coordinate system given in Fig. 1. The integration is over the space of the electron 1, and

$$\sigma(\mathbf{r}; \mathbf{z}_A) \equiv N \int \Psi_0 \Psi d\mathbf{r}_2 \dots d\mathbf{r}_N / \int \Psi_0 \Psi d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (18)$$

which we shall call the transition density hereafter. Now from

Eq. (17), the derivative may be written by

$$E^{(k)} = (-1)^k k! \left[ \frac{\gamma_A \gamma_B}{R_0^{k+1}} + (-1)^{k-1} \gamma_A \sum_{l=0}^{k-1} \binom{k}{l} \left[ \frac{\partial^{k-l}}{\partial z_A^{k-l}} \cdot \int \frac{1}{r_A} \sigma^{(l)}(\mathbf{r}) d\mathbf{r} \right]_{z_A=0} \right] \quad (19)$$

where

$$\sigma^{(l)}(\mathbf{r}) \equiv \left[ \frac{\partial^l}{\partial z_A^l} \sigma(\mathbf{r}; \mathbf{z}_A) \right]_{z_A=0}, \quad \sigma^{(0)}(\mathbf{r}) \equiv \rho^{(0)}(\mathbf{r}) \quad (20)$$

Through a manipulation similar to that presented in A, one obtains

$$E^{(k)} = (-1)^k k! \left[ \frac{\gamma_A \gamma_B}{R_0^{k+1}} + (-1)^{k-1} \gamma_A \sum_{m=0}^{k-1} \frac{1}{m!} \left[ \int \frac{P_{k-m}(\omega\theta)}{r^{k-m+1}} \sigma^{(m)}(\mathbf{r}) d\mathbf{r} - \sum_{q=0}^{k-m-2} \frac{(q+1)(2k-2m-3-2q)}{(q+2)!(2k-2m-1-q)} \int \frac{P_{k-m-q-2}(\omega\theta)}{r^{k-m-q}} \delta(r) \sigma^{(q)}(\mathbf{r}) d\mathbf{r} \right] \right] \quad (21)$$

For  $k=1$ , Eq. (21) gives Eq. (11), and for  $k=2$  and 3, one has<sup>15</sup>

$$E^{(2)} = 2 \frac{\gamma_A \gamma_B}{R_0^3} - 2 \gamma_A \int \frac{P_2(\omega\theta)}{r^3} \rho^{(0)}(\mathbf{r}) d\mathbf{r} + \frac{\gamma_A}{3} \int \frac{\delta(r)}{r^2} \rho^{(0)}(\mathbf{r}) d\mathbf{r} - 2 \gamma_A \int \frac{P_1(\omega\theta)}{r^2} \sigma^{(1)}(\mathbf{r}) d\mathbf{r} \quad (22)$$

$$E^{(3)} = -6 \frac{\gamma_A \gamma_B}{R_0^4} + 6 \gamma_A \int \frac{P_3(\omega\theta)}{r^4} \rho^{(0)}(\mathbf{r}) d\mathbf{r} - \frac{9}{5} \gamma_A \int \frac{P_1(\omega\theta)}{r^3} \delta(r) \rho^{(0)}(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \gamma_A \int \frac{\delta^{(1)}(r)}{r^2} \rho^{(0)}(\mathbf{r}) d\mathbf{r} + 6 \gamma_A \int \frac{P_2(\omega\theta)}{r^3} \sigma^{(1)}(\mathbf{r}) d\mathbf{r} - \gamma_A \int \frac{\delta(r)}{r^2} \sigma^{(1)}(\mathbf{r}) d\mathbf{r} + 3 \gamma_A \int \frac{P_1(\omega\theta)}{r^2} \sigma^{(2)}(\mathbf{r}) d\mathbf{r} \quad (23)$$

### III. Discussion

Suppose that <sup>3,4</sup>

$$\rho = \rho_A + \rho_B + \rho_D \quad (24)$$

where (i) the  $\rho_A$  is the part of  $\rho$  which is spherical around the nucleus A and follows rigidly A without deformation, and (ii) the  $\rho_B$  is the corresponding density which follows B and in addition, vanishes in the vicinity of A and at the left of A at the equilibrium separation (see Fig. 1), and (iii) the  $\rho_D$  is the rest of  $\rho$ . Now the  $\rho_A$  does not contribute to the force according to Eq. (2) and consequently does not contribute to  $E^{(k)}$  for any k. Also, for the coordinate system given Fig. 1,

$$\int h(\underline{r}) \delta^{(m)}(\underline{r}) \rho_B^{(n)} dT = 0 \quad \text{for an arbitrary function } h(\underline{r}), \text{ and}$$

$$\rho_B^{(0)} = \rho_B, \rho_B^{(1)} = \rho_B^{(2)} = \dots = 0.$$

For instance, from Eqs. (12) and (13),

$$\frac{\gamma_A}{3} \int \frac{\delta(r)}{r^2} \rho_A^{(0)}(r) dT - \gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_A^{(1)}(r) dT = 0 \quad (25)$$

$$-\frac{\gamma_A}{2} \int \frac{\delta^{(1)}(r)}{r^2} \rho_A^{(0)}(r) dT + 4\gamma_A \int \frac{P_2(uR\theta)}{r^3} \rho_A^{(1)}(r) dT - \frac{2}{3}\gamma_A \int \frac{\delta(r)}{r^2} \rho_A^{(1)}(r) dT$$

$$+ \gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_A^{(2)}(r) dT = 0 \quad (26)$$

and

$$\frac{\gamma_A}{3} \int \frac{\delta(r)}{r^2} \rho_B^{(0)}(r) dT = -\gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_B^{(1)}(r) dT = 0 \quad (27)$$

$$-\frac{\gamma_A}{2} \int \frac{\delta^{(1)}(r)}{r^2} \rho_B^{(0)}(r) dT = 4\gamma_A \int \frac{P_2(uR\theta)}{r^3} \rho_B^{(1)}(r) dT = -\frac{2}{3}\gamma_A \int \frac{\delta(r)}{r^2} \rho_B^{(1)}(r) dT$$

$$= \gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_B^{(2)}(r) dT = -\frac{9}{5}\gamma_A \int \frac{P_1(uR\theta)}{r^3} \delta(r) \rho_B^{(0)}(r) dT = 0 \quad (28)$$

where Eqs. (25) and (27) are originally due to Salem<sup>3</sup>.

From Eqs. (12) and (13), one can say that there is an extensive cancellation between terms involving the charge density and its derivatives<sup>16</sup>. In fact the recent calculation of  $E^{(3)}$  of the  $H_2$  molecule by Benston et. al. shows<sup>17</sup>

$$\langle \psi_0 | H_2 | \psi_0 \rangle + \psi_1 \text{ terms} = -1.21 \text{ (a.u.)} \quad (29)$$

(-5.12)      (3.91)

Now from Eq. (9), one can write

$$E^{(K)} = (-1)^K K! \frac{\gamma_A \gamma_B}{R_0^{K+1}} - (-1)^K K! \gamma_A \int \frac{P_K(uR\theta)}{r^{K+1}} (\rho_B^{(0)}(r) + \rho_D^{(0)}(r)) dT + Q_D^{(K)} \quad (30)$$

where  $Q_D^{(K)}$  contains only  $\rho_D$ . For example,

$$Q_D^{(2)} = \frac{\gamma_A}{3} \int \frac{\delta(r)}{r^2} \rho_D^{(0)}(r) dT - \gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_D^{(1)}(r) dT \quad (31)$$

and

$$Q_D^{(3)} = -\frac{9}{5} \gamma_A \int \frac{P_1(uR\theta)}{r^3} \delta(r) \rho_D^{(0)}(r) dT - \frac{\gamma_A}{2} \int \frac{\delta^{(1)}(r)}{r^2} \rho_D^{(0)}(r) dT + 4\gamma_A \int \frac{P_2(uR\theta)}{r^3} \rho_D^{(1)}(r) dT - \frac{2}{3} \gamma_A \int \frac{\delta(r)}{r^2} \rho_D^{(1)}(r) dT + \gamma_A \int \frac{P_1(uR\theta)}{r^2} \rho_D^{(2)}(r) dT \quad (32)$$

A possible approximation may be to neglect  $\rho_D$  entirely,<sup>18,3,4</sup> thus,

$$E^{(K)} \doteq (-1)^K K! \frac{\gamma_A \gamma_B}{R_0^{K+1}} - (-1)^K K! \gamma_A \int \frac{P_K(uR\theta)}{r^{K+1}} \rho_B^{(0)}(r) dT$$

$$= \gamma_A \frac{(-1)^K K!}{R_0^{K+1}} \left[ \gamma_B - \int \rho_B^{(0)}(r) dT \right] \quad (33)$$

If this is done, however, the following contradictions occur:

(a)  $E^{(1)} \neq 0$  even when  $R_0$  is the equilibrium separation unless

$$\gamma_B = \int \rho_B^{(0)}(r) dT, \text{ which means 100\% screening.}$$

(b) It was shown that empirically<sup>3</sup> one has

$$E^{(2)} \doteq \gamma_A q_A, \quad q_A \equiv 2\gamma_B \left( \frac{1}{R_0^3} - \int \frac{P_2(uR\theta)}{r^3} \rho_B^{(0)}(r) dT \right) \quad (34)$$

where  $q_A$  is the nuclear electric quadrupole coupling constant,



but it is also known that the most important contribution to comes from  $P_z^2$  density centered at the atom A if one uses molecular orbital description<sup>19</sup>. However,  $P_z^2$  belongs to  $P^{(0)}$  which Eq. (33) neglects.

(c) The ratio of the electronic and the nuclear charge contributions to  $E^{(k)}$  is given, according to Eq. (33), by  $\frac{E_e^{(k)}}{E_N^{(k)}} = \text{constant}$  which is not realistic, as Schwendeman<sup>4</sup> pointed out.

A compromise may be to neglect  $Q_D^{(k)}$  and retain the integral  $\int \frac{P_k(\cos\theta)}{r^{k+1}} P_D^{(0)}(z) d\tau$  in Eq. (30), giving<sup>20</sup>

$$E^{(k)} \doteq (-1)^k k! \frac{\gamma_A \gamma_B}{R_0^{k+1}} - (-1)^k k! \gamma_A \int \frac{P_k(\cos\theta)}{r^{k+1}} P^{(0)}(z) d\tau \quad (35)$$

For  $k=1$ , Eq. (35) is exact. For  $k=2$ , one has  $E^{(2)} \doteq \gamma_A q_A$ . For  $k=3$ , one has

$$E^{(3)} \doteq -6 \frac{\gamma_A \gamma_B}{R_0^4} + 6 \gamma_A \int \frac{P_3(\cos\theta)}{r^4} P^{(0)}(z) d\tau \quad (36)$$

With the Wang function ( $R_0 = 1.45$ , the orbital exponent  $\gamma = 1.159$  according to ref.21), Eq.(36) gives

$$E^{(3)} \doteq -1.357 + 0.146 = -1.21 \text{ (a.u.)} \quad (\text{Exp. Val.} = -1.30 \text{ a.u.}) \quad (37)$$

for the  $H_2$  molecule (see Eq. (29) for comparison).

Although the plausibility of the approximation given by Eq. (36) (or in general Eq. (35)) is subjected to further numerical checks, at this point however one may conjecture Eq. (36) as (approximate) working formula for  $E^{(3)}$ .

Now it may be instructive to note that the part of the transition density which is symmetrical with respect to the plane passing  $(0,0, \frac{z_A}{2})$  and perpendicular to the internuclear axis, say  $\sigma_z$ ,

does not contribute to the energy change according to Eq. (17). Therefore  $E^{(k)}$  does not include any contribution from  $\sigma_s$ . Furthermore the part of  $\sigma$  which does not change, say  $\sigma_B$ , gives  $\sigma_B^{(1)} = \sigma_B^{(2)} = \dots = 0$ . For such part of the transition density, then the integral  $\int \frac{P_n(uR\theta)}{r^m} \sigma_B^{(k)} dT = 0$  for  $k \geq 1$ . In fact, for an infinitesimal change of the internuclear separation, one sees that  $\sigma_s \rightarrow \rho_A$  and  $\sigma_B \rightarrow \rho_B$ . However, since the transition density is defined only after description of the molecular wave function is given, it may not be meaningful physically as the ordinary charge density  $\rho$ .

It is known that the Hellmann Feynman theorem given by Eq. (1), upon which the present derivation of Eq. (9) is based is highly sensitive to the error in wave function employed. Indeed, with the variational wave function  $\tilde{\Phi}$ , which satisfies  $\langle \tilde{\Phi} | H - E | \tilde{\Phi} \rangle = 0$ , the correct expression is

$$\frac{dE}{dR} = \langle \tilde{\Phi} | \frac{\partial H}{\partial R} | \tilde{\Phi} \rangle + \left[ \langle \tilde{\Phi} | H | \frac{\partial \tilde{\Phi}}{\partial R} \rangle + \langle \frac{\partial \tilde{\Phi}}{\partial R} | H | \tilde{\Phi} \rangle \right] \quad (38)$$

where the term with the square bracket [ ] does not vanish in general. The prescription of the "stable wave function"<sup>12</sup>, which, by definition, satisfies

$$\frac{dE}{dR} = \langle \tilde{\Phi} | \frac{\partial H}{\partial R} | \tilde{\Phi} \rangle \quad (39)$$

is well summarized by Schwendeman<sup>4</sup>. Thus avoiding the further discussion on this matter here, we just like to give a new prescription of a stable function in the following.

From Eq. (17), which is the Integral Hellmann Feynman theorem<sup>7,8,9</sup>

one can derive the Hellmann Feynman theorem, without employing the condition<sup>22</sup>  $(H-E)\tilde{\Psi} = (H_0-E_0)\tilde{\Psi}_0 = 0$ . Therefore one can say that if

$$\tilde{E} - E_0 = \frac{\langle \tilde{\Psi} | H - H_0 | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi} | \tilde{\Psi}_0 \rangle} \quad (40)$$

then Eq. (39) is rigorously valid, or i.e., that  $\tilde{\Psi}$  is a stable wave function. Actually, Epstein<sup>9</sup> found that if the variational wave functions  $\tilde{\Psi}$  and  $\tilde{\Psi}_0$  are made of a common basis set, then Eq. (40) is satisfied. Furthermore, it is now apparent that Eq. (21) is also the rigorous representation of if Eq. (40) is satisfied.

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REFERENCES AND FOOTNOTES

1. H. Hellmann, Einführung in die Quantenchemie (Franz Deuticke, Leipzig (1937)), p. 285.  
R. P. Feynman, Phys. Rev. 56, 340 (1939).
2. T. Berlin, J. Chem. Phys. 19, 208 (1951).
3. L. Salem, J. Chem. Phys. 38, 1227 (1963).
4. R. H. Schwendeman, J. Chem. Phys. 44, 556 (1966).
5. W. Byers Brown, Proc. Cambridge Phil. Soc. 54, 251 (1958).
6. W. L. Clinton, J. Chem. Phys. 33, 1603 (1960); 36, 555, (1962); 38, 2339 (1963).
7. R. G. Parr, J. Chem. Phys. 40, 3726 (1964).
8. H. J. Kim and R. G. Parr, J. Chem. Phys. 41, 2892 (1964).
9. R. E. Wyatt and R. C. Parr, J. Chem. Phys. 44, 1529 (1966).
10. In ref. 4, the crucial integral is

$$\frac{\partial^k}{\partial z_A^k} \int \rho(\underline{r}_A; z_A) \frac{\cos \theta}{r_A^2} d\tau = \int \frac{\partial^k \rho(\underline{r}_A; z_A')}{\partial z_A'^k} \frac{\cos \theta_A}{r_A^2} d\tau, \quad z_A' \equiv z_A$$

11. W. A. Bingel, J. Chem. Phys. 30, 1254 (1959)

The author wishes to express appreciation to Prof. W. Byers Brown who gave his own derivation (unpublished) of Eq. (5) in the text.

12. G. G. Hall, Phil. Mag. 6, 249 (1961).
13. A. Messiah, Quantum Mechanics Vol. I. (John Wiley & Sons, New York).
14.  $\frac{\gamma_A}{3} \int \frac{\delta(r)}{r^2} \rho^{(0)}(r) d\tau = \frac{4\pi}{3} \gamma_A \rho^{(0)}(A)$  where  $\rho^{(0)}(A)$  is the electronic charge density at the nucleus A.

15. Expanding

$$H = \sum_K \frac{(\Delta R)^K}{K!} H^{(K)}, \quad E = \sum_K \frac{(\Delta R)^K}{K!} E^{(K)}, \quad \Phi = \sum_K \frac{(\Delta R)^K}{K!} \Phi^{(K)}$$

one can show that

$$\sigma^{(1)}(\underline{x}) = \frac{1}{2} \rho^{(1)}(\underline{x}), \quad \sigma^{(2)}(\underline{x}) = \frac{1}{2} \left[ \rho^{(2)}(\underline{x}) - N \int \Phi^{(1)} \Phi^{(1)} dT_2 \dots dT_N \right]$$

Furthermore if one assumes  $\langle \Phi_0 | \Phi \rangle = 1$  then

$$\int g(\underline{x}) \sigma^{(m)}(\underline{x}) dT = (-1)^m \int \sum_i^N g(\underline{x}_i) \Phi_0 \Phi^{(m)} dT_1 dT_2 \dots dT_N$$

16. Comparing Eqs. (12) and (13) with (22) and (23), one also sees that the cancellation occurs among terms involving the derivatives of the transition density.
17. M. L. Benston and B. Kirtman, J. Chem. Phys. 44, 126 (1965).
- The calculation is based on the variation-perturbation treatment.
  - The data is from the case where  $\psi_0$  is Wang function with  $R_0 = 1.41$
  - $H_3$  is defined by  $\left( \frac{\partial^3 H}{\partial R^3} \right)_{R=R_0}$  and  $-5.12$  for  $\langle \psi_0 | H_3 | \psi_0 \rangle$  is the "empirical value" due to the virial theorem.
18. S. Bratoz, R. Daudel, M. Roux, and M. Allavena, Rev. Mod. Phys. 32, 412 (1960).
19. T. M. Sugden and C. N. Kennedy, Microwave Spectroscopy of Gases, CH. 6. (van Nostrand, London (1965)).
20. 
$$\int \frac{P_K(\underline{x}, \underline{R})}{V^{K+1}} \rho_A^{(0)}(\underline{x}) dT = 0 \quad \text{for } K \geq 1$$
21. J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. 18, 130 (1950).
22. In fact, one needs Eqs. (14) and (15) in order to derive Eq. (17). But the point is that the derivation of Eq. (1) from Eq. (17) does not require anymore Eqs. (14) and (15).

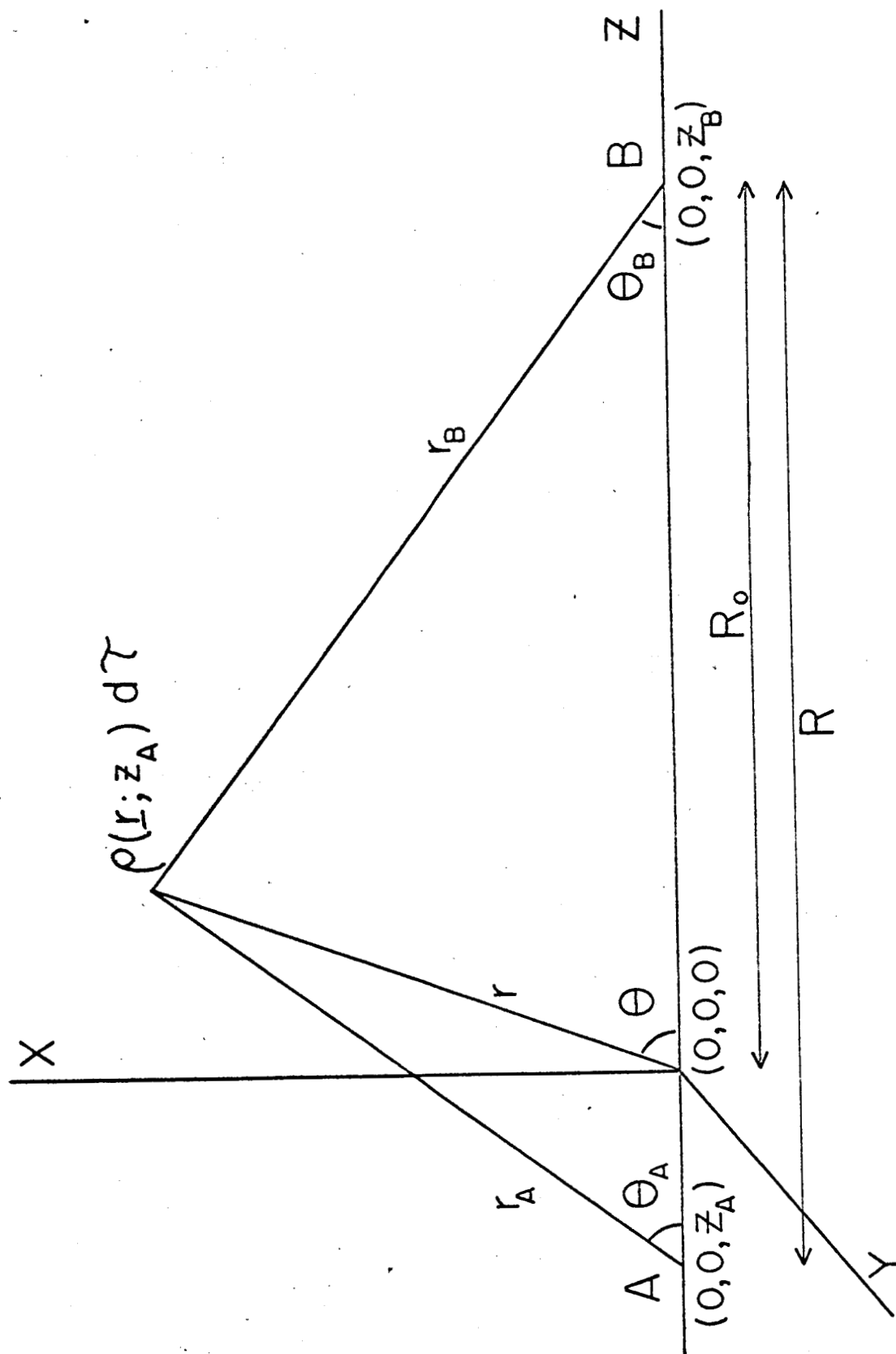


Figure 1. The coordinate system.  $B$  is fixed to the coordinate frame.